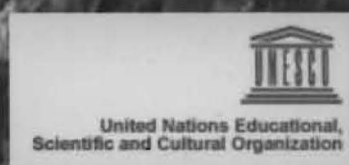


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ANTHROPOGENIC EFFECTS ON THE HUMAN ENVIRONMENT IN THE TERTIARY BASINS IN THE MEDITERRANEAN PROCEEDINGS

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PHASE COMPOSITION OF THE SLAG OF THE FENI INDUSTRY METALLURGICAL PLANT AND ITS IMPACT ON THE ENVIRONMENT

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ABSTRACT

Industrial waste dumps pose a great risk to the human environment, particularly if they are located close to settlements, the amount of the material disposed is large, if the composition of the material poses risk to the system of ground waters, if they cause aerial pollution etc.

The waste dump near the Feni Industry Company is located in the vicinity of the village of Vozarci, Kavadarci where about ten million tons of waste material has been dumped. The present authors carried out investigations on the phase state of the slag. Based on the composition of the slag a review has been given on its impact on the human environment.

INTRODUCTION

The Feni Industry metallurgical company is situated some 7 km from Kavadarci and is the only producer of iron-nickel in the Republic of Macedonia. The company processes about 700 000 tones of nickeliferous-iron ore mined in the Rzanovo deposit (Boev 1996, Boev et al., 1995). Recently the company also started processing nickeliferous ore imported from Albania and Indonesia.

Large amount of slag, which during the liquid state flows into the dump close to Vozarci (Fig.1), comes from the pyrometallurgical technological process for obtaining iron- nickel. It is worth noting also that the dump contains large amounts of slag that come from the furnace and from the converter. Investigation on the phase state of the slag is important from the point of view of its impact on the human environment. So far, several papers have been published in connection with the phase state of the ore and that of the prereduced materials (Boev et. al.1992, 1994).

METHOD OF WORK

Method of work included as follows:

- collection of samples from the furnace,
- preparation of samples for reflected polarized light,
- microscopic determination of mineral phases that can be seen under a microscope by the use of the method of reflected polarized light,

- scanning electronic microscopy and determination of mineral phases,
- chemical examinations by FUS-ICP, INAA, TD-ICP of the slag in terms of the presence of macro and microelements.



Fig.1. Panoramic view of the waste dumps of Feniindustri

RESULTS AND DISCUSSION

Five slag samples were collected from the electrical furnace of Feni Industry and worked by optic microscopic methods. During the analyses several mineral phases were determined for all 5 samples (in most cases three visible phases in the microscope): silicate, spinel and metal phases.

Silicate phase is the most frequent and dominant, the second is the spinel phase and the last, with the amount of 0.8 – 1%, is the metal phase. Based on microscopic features, particularly by the occurrence mode, it can be said that the spinel phase, most probably, is magnetite. The paper will present a number of photos of mineral phases present (figs. 2 and 3).

Scanning electronic microscope was used for the determination of semi-quantitative composition of mineral phases. The results speak for the composition of mineral phases (Table 1, fig. 4)

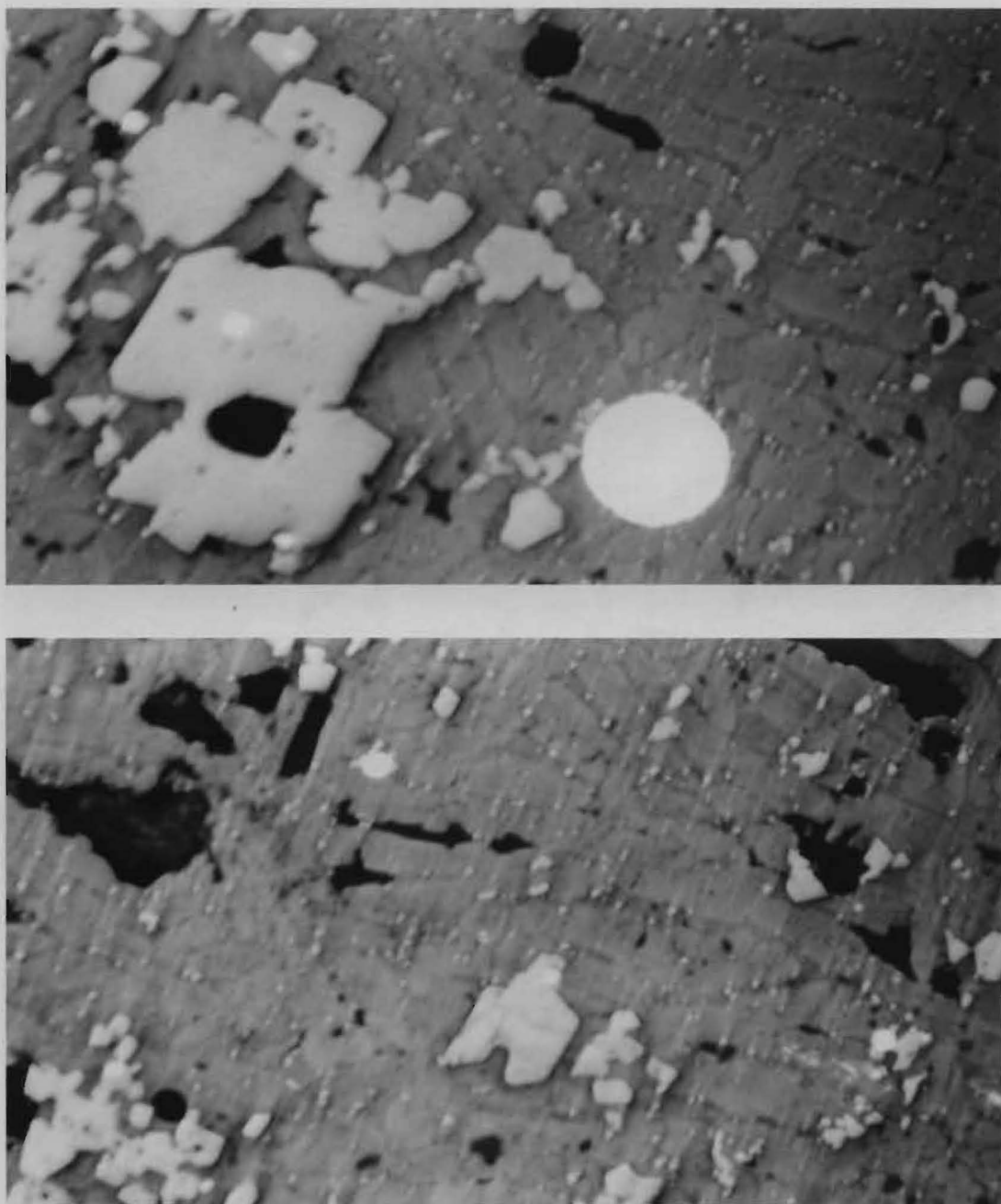


Fig. 2. Microscopic photo (ball shapes – metal phase; regular shapes – spinel phase; other- silicate phase (Nx8ob))

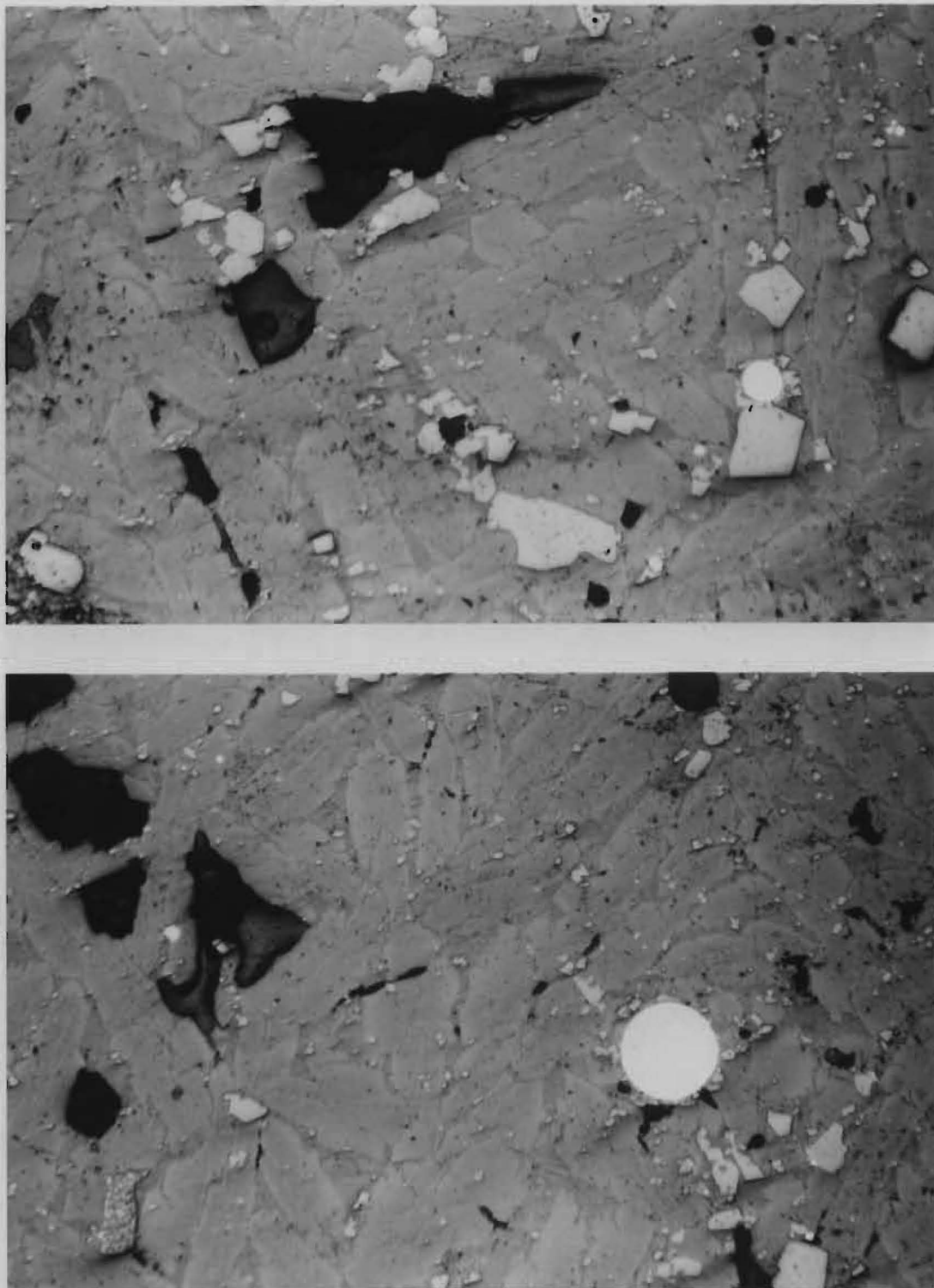


Fig. 3. Microscopic photo (dark balls – removed metal phases during polishing; regular shapes - spinel phase , light balls - metal phase)

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Table 1: Semi-quantitative analysis of metallurgical slag from Feniindustry

Element	App	Intesity	Weight %	Weight %	Atomic %
	Conc.	Corrn.		Sigma	
C K	0.19	0.3972	9.76	5.00	17.76
O K	2.14	1.1156	39.20	3.17	53.52
Mg K	0.17	0.6481	5.26	0.93	4.72
Al K	0.07	0.7196	2.04	0.72	1.66
Si K	0.51	0.8065	12.95	1.21	10.07
Ca K	0.10	1.0229	1.95	0.83	1.06
Fe K	1.07	0.8639	25.23	2.61	9.87
Ni K	0.15	0.8402	3.60	3.42	1.34
Totals			100.00		

Table 2:

Element	App	Intesity	Weight %	Weight %	Atomic %
	Conc.	Corrn.		Sigma	
C K	0.26	0.4032	13.28	3.31	22.65
O K	2.02	1.0419	40.34	1.99	51.68
Mg K	0.17	0.6880	5.23	0.58	4.41
Al K	0.07	0.7515	1.85	0.46	1.41
Si K	0.57	0.8323	14.27	0.80	10.41
Ca K	0.08	1.0127	1.73	0.56	0.89
Fe K	0.94	0.8441	23.30	1.65	8.55
Ni K					
Totals			100.00		

Table 3:

Element	App	Intesity	Weight %	Weight %	Atomic %
	Conc.	Corrn.		Sigma	
C K					
O K	2.28	1.3668	4.68	0.91	12.56
Mg K	0.88	0.5023	4.96	0.66	8.76
Al K					
Si K	3.13	0.7294	12.05	0.73	18.43
Ca K					
Fe K	26.72	0.9599	78.01	1.21	60.25
Ni K	0.05	0.7521	0.3	1.42	1.32
Totals			100.00		

Table 4:

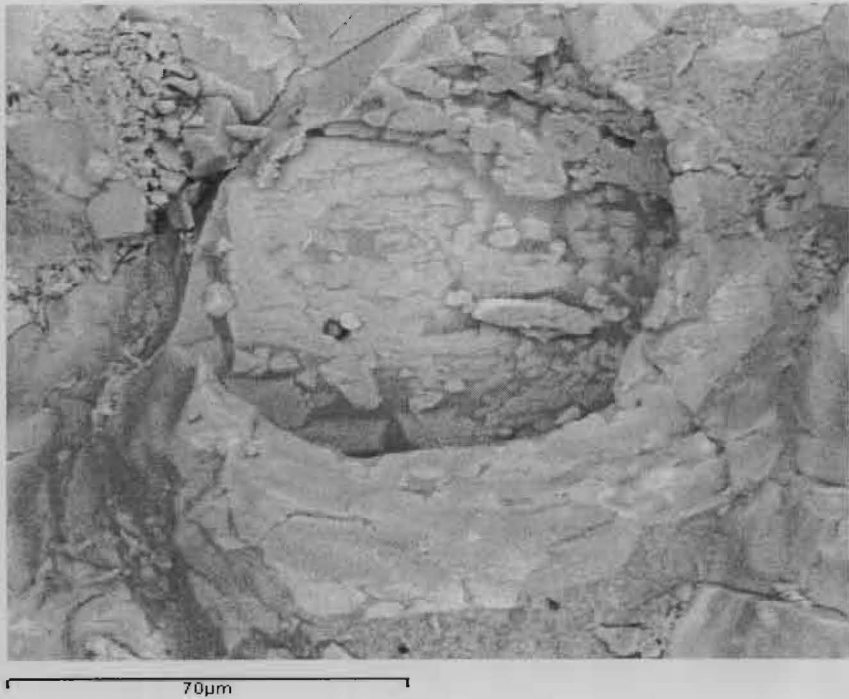
Element	App	Intesity	Weight %	Weight %	Atomic %
	Conc.	Corrn.		Sigma	
C K	0.83	0.4641	5.23	2.12	18.67
O K	1.52	1.3712	3.25	0.80	8.71
Mg K	0.22	0.4602	1.40	0.49	2.46
Al K					
Si K	0.23	0.7118	0.96	0.35	1.47
Ca K	0.36	1.1644	0.91	0.36	0.97
Fe K	29.06	0.9708	87.78	2.24	67.34
Cr K	0.20	1.2391	0.47	0.53	0.39
Totals			100.00		

Table 5:

Element	App Conc.	Intesity Corn.	Weight %	Weight % Sigma	Atomic %
Fe K	4.40	1.000	100.00	0.01	100.00
Cr K					
Totals			100.00		

Table 6:

Element	App Conc.	Intesity Corn.	Weight %	Weight % Sigma	Atomic %
B K	0.32	0.1384	40.36	7.60	56.72
O K	1.88	0.9451	34.80	4.53	33.05
Mg K	0.20	0.7945	4.42	0.67	2.76
Al K	0.03	0.8354	0.55	0.31	0.31
Si K	0.32	0.9085	6.20	0.86	3.35
Ca K	0.05	1.0193	0.79	0.43	0.30
Fe K	0.61	0.8260	12.89	1.98	3.51
Totals			100.00		



Site 6

Fig.4. Scaning electron microscope pictures of the slag

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Table 7:

Element	App	Intesity	Weight %	Weight %	Atomic %
	Conc.	Cornn.		Sigma	
B K	0.24	0.0868	41.91	145.24	71.42
Al K	0.93	0.9065	15.53	39.00	10.60
Si K	0.65	0.8248	11.90	30.04	7.80
VK	0.09	0.9167	1.52	8.95	0.55
Fe K	1.68	0.8712	29.15	73.54	9.62
Totals			100.00		

Table 8:

Element	App	Intesity	Weight %	Weight %	Atomic %
	Conc.	Cornn.		Sigma	
O K	1.40	1.5460	1.44	0.53	4.84
Al K	0.16	0.5623	0.47	0.31	0.92
Ca K	0.43	1.1859	0.57	0.29	0.77
Fe K	59.15	0.9952	94.61	1.57	90.84
Cr K	0.13	1.2887	0.16	0.51	0.16
Co K	1.88	0.9774	3.07	1.38	2.79
Totals			100.00		

Table 9:

Element	App	Intesity	Weight %	Weight %	Atomic %
	Conc.	Cornn.		Sigma	
C K	0.28	0.4394	6.07	6.40	14.94
O K	3.21	1.3982	22.24	3.06	41.09
Mg K	0.14	0.5226	2.68	1.36	3.26
Al K	0.13	0.6327	1.93	1.06	2.12
Si K	0.43	0.7436	5.57	1.15	5.87
Cr K	0.10	1.1237	0.86	1.71	0.49
Fe K	6.24	0.9199	65.67	6.62	34.76
Co K	-0.13	0.9017	-1.44	3.98	-0.72
Ni K	-0.32	0.8655	-3.58	4.84	-1.80
Totals			100.00		

Table 10:

Element	App	Intesity	Weight %	Weight %	Atomic %
	Conc.	Cornn.		Sigma	
O K	2.35	1.4911	41.01	28.22	64.11
Al K	0.32	0.7267	11.52	9.15	10.68
Si K	0.26	0.7409	9.07	7.76	8.08
Fe K	1.14	0.8840	33.96	25.13	15.21
Co K	0.17	0.8658	5.05	18.20	2.14
Ga K	-0.02	0.8489	-0.61	61.27	-0.22
Totals			100.00		

Tables 1 to 10 show semi quantitative analyses of the slag from the electric furnace.

The scanning electronic microscopy has also determined three major phases in the slag from the electric furnace: silicate phase was found in the amount of 84%, then the spinel phase of some 15% and metal phase averaged at 0.9 to 1%.

It must also be said that, for better defining of quantitative relations of individual phases, a number of examinations are necessary and that data obtained can be taken as provisional. The size of the phase can be defined in the interval from several micrometers up to 100 micrometers.

Based on analyses by scanning electronic microscope it can be inferred that spinel phase does not contain large nickel concentrations (some 0.3%), that the silicate phase contains fairly low concentrations of nickel (about 0.01%) and also that in such cases they are microcrystal aggregates of spinels scattered over the silicate phase.

It should be mentioned that the exposition time is short and in the future detailed determination of phases must be carried out. However, these results, essentially, are a good guide for future investigations and, as such, may serve as good directions in investigations.

The metal phase in the slag of the electric furnace, seen under a microscope as small balls or irregular balls, is of interest and should be studied in future. Namely, the phase, in some cases, is relatively pure and contains large iron concentrations. In some cases it also contains 3.50% nickel. It should be mentioned that there are several types of ball phases that possess different composition when ball phases are investigated more thoroughly.

Based on these preliminary investigations it can be inferred that nickel present in the slag of the electric furnace is within 0.08 and 0.13% (taking in consideration errors occurred during the short time of exposition in scanning electronic microscopy).

It is important to mention here that in some cases vanadium, gallium and boron were noticed. This leads to the assumption that the slag of the electric furnace of Feni Industry should be studied for possible presence of trace elements and rare earths.

Chemical and geochemical analyses by ICP and methods of instrumental neutron activation were carried out on the samples. The results obtained are shown in Table 11.

From the data presented, it can be inferred that the material is rich in iron, silicium, aluminum, magnesium and calcium. Sulphur content is low (about 0.1%) and does not pose a risk to human environment.

Data also indicate that the material has no microelements that may pose risk to the human environment (cadmium amount is slightly increased). pH value amounts to 7 and can be said that it is a neutral medium.

Liquid samples, the so called leaching test, have also been taken from the material. The analyses yielded data that do not indicate the possibility of greater extraction of some components from the slag in external conditions. The test has proved that the material does not pose risk to the human environment in terms of possible contamination.

Table 11: Chemical and geochemical composition of the slag from
Finiindustry.

elements	method	limit	T-1	T-2	T-3	T-4	T-5
SiO ₂ (%)	FUS-ICP	0.01	34.85	34.99	35.19	34.88	34.64
Al ₂ O ₃ (%)	FUS-ICP	0.01	4.68	4.59	4.62	4.58	4.53
Fe ₂ O ₃ (T)%	FUS-ICP	0.01	45.69	45.66	45.55	46.12	46.56
MnO (%)	FUS-ICP	0.01	0.574	0.576	0.579	0.576	0.573
MgO (%)	FUS-ICP	0.01	12.99	13.1	13.19	13.04	12.97
CaO (%)	FUS-ICP	0.01	3.63	3.85	3.84	3.78	3.76
Na ₂ O(%)	FUS-ICP	0.01	0.32	0.34	0.33	0.33	0.33
K ₂ O (%)	FUS-ICP	0.01	0.23	0.22	0.26	0.22	0.24
TiO ₂ (%)	FUS-ICP	0.01	0.113	0.116	0.116	0.115	0.113
P ₂ O ₅ (%)	FUS-ICP	0.01	0.01	0.01	0.02	0.01	0.02
LOI (%)	FUS-ICP	0.01	<0.01	<0.01	<0.01	<0.01	<0.001
Total			98.62	98.92	99.15	99.09	99.19
Au (ppb)	INAA	2	<2	<2	<2	<2	<2
Ag (ppm)	TD-ICP	0.5	2.5	2.2	2.2	2.2	2.6
As (ppm)	INAA	1	<1	<1	<1	<1	<1
Ba (ppm)	FUS-ICP	3	78	80	81	79	79
Be (ppm)	FUS-ICP	1	<1	<1	<1	<1	<1
Bi (ppm)	TD-ICP	2	<2	<2	<2	<2	<2
Br (ppm)	INAA	0.5	<0.5	<0.5	0.7	0.8	1.4
Cd (ppm)	TD-ICP	0.5	1.7	1.6	1.5	1.6	1.8
Co (ppm)	INAA	0.1	119	110	118	122	135
Cr (ppm)	INAA	0.5	25000	26000	30000	31000	29000
Cs (ppm)	INAA	0.2	4.3	5.1	4.6	5	4.7
Cu (ppm)	TD-ICP	1	14	14	15	15	15
Hf (ppm)	INAA	0.2	<0.2	<0.2	0.5	<0.2	0.8
Hg (ppm)	INAA	1	<1	<1	<1	<1	<1
Ir (ppb)	INAA	1	<1	<1	<1	<1	<1
Mo (ppm)	INAA	2	<2	<2	<2	<2	<2
Ni (ppm)	TD-ICP	1	864	537	844	767	696
Pb (ppm)	TD-ICP	5	12	12	16	9	9
Rb (ppm)	INAA	10	30	30	<10	<10	40
S (%)	TD-ICP	0.001	0.14	0.132	0.119	0.146	0.169
Sb (ppm)	INAA	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sc (ppm)	INAA	0.01	42.5	43.8	45	43.4	44.5
Se (ppm)	INAA	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Sr (ppm)	FUS-ICP	2	173	178	179	178	176
Ta (ppm)	INAA	0.3	0.6	<0.3	<0.3	<0.3	<0.3
Th (ppm)	INAA	0.1	1.4	1.7	1.5	1.7	1.7
U (ppm)	INAA	0.1	0.8	<0.1	0.8	1.1	0.9
V (ppm)	FUS-ICP	5	158	152	154	153	152
W (ppm)	INAA	1	9	10	6	6	5
Y (ppm)	FUS-ICP	1	4	5	5	4	4
Zn (ppm)	TD-ICP	1	72	202	186	151	130
Zr (ppm)	FUS-ICP	4	33	33	35	33	34
La (ppm)	INAA	0.05	4.28	4.45	4.78	4.53	4.72
Ce (ppm)	INAA	1	14	14	14	14	18
Nd (ppm)	INAA	1	<1	4	<1	<1	3
Sm (ppm)	INAA	0.01	0.76	0.86	0.82	0.78	0.80
Eu (ppm)	INAA	0.05	0.14	0.36	0.22	0.16	0.16
Tb (ppm)	INAA	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Yb (ppm)	INAA	0.05	0.4	0.41	0.47	0.44	0.42
Lu (ppm)	INAA	0.01	0.06	0.06	0.07	0.06	0.06
pH			7.1	6.9	7.2	7.0	6.9

Conclusion

Based on investigations carried out on the mineral and chemical composition of the slag of the Feni Industry metallurgy waste dump it can be inferred that both chemical and mineralogical compositions do not pose a risk to the environment and the mineral composition does not pose limitation with regard to the use of the material in construction or bulk material for covering of roads.

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